

AD 748103

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June 30, 1970 - June 30, 1972

ARPA Order Number 1482 Ande 2
Program Code Number OB20

Name of Grantee:
COLUMBIA UNIVERSITY
New York, New York 10027

Effective Date of Grant:
30 JUNE 1970

Grant Number:
DA-ARO-D-31-124-70-C103

Amount of Grant:
\$ 50,000

Principal Investigator:
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(212) 280-2017

Short Title of Work:
METAL OXIDE INFRARED EMISSION

Sponsored by:
ADVANCED RESEARCH PROJECTS AGENCY
ARPA Order No. 1482 Ande 2

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I. LIST OF PUBLICATIONS PRODUCED (in chronological order)

1. C. D. Jonah and R. N. Zare, "Formation of Group IIA Dihalides By Two-Body Radiative Association" *Chem. Phys. Letters* 9, 65 (1971).
2. C. D. Jonah, R. N. Zare, and Ch. Ottlinger, "Crossed-Beam Chemiluminescence of Some Group IIA Metal Oxides" *J. Chem. Phys.* 56, 263 (1972).
3. A. Schultz, H. W. Cruse, and R. N. Zare, "Laser-Induced Fluorescence: A Method to Measure the Internal State Distribution of Reaction Products," *J. Chem. Phys.* (accepted for publication).
4. J. L. Gole and R. N. Zare, "Determination of D_0^0 (ΔE) from Crossed-Beam Chemiluminescence of $M + O_3$ " *J. Chem. Phys.* (accepted for publication).

II. LIST OF PARTICIPATING PERSONNEL

Name	Position	Present Address
Dr. C. D. Jonah	Postdoctoral	Argonne National Laboratory
Dr. A. Schultz	Postdoctoral	Fakultät für Physik der Universität Freiburg, Germany
Dr. H. W. Cruse	Postdoctoral	Department of Chemistry Columbia University
Dr. J. L. Gole	Postdoctoral	Department of Chemistry Columbia University
Prof. R. N. Zare	Principal Investigator	Department of Chemistry Columbia University

III. SUMMARY AND HIGHLIGHTS

A. Objective

The state of the earth's upper atmosphere under disturbed conditions is of considerable importance for a variety of military applications ranging from artificial metal releases to high-altitude nuclear explosions. In this context, we have been developing new techniques for determining the structure of metal oxide molecules and for monitoring their production kinetics. Emphasis has been placed on those properties that control the infrared emission of metal oxides that are of special interest to ARPA.

B. Experimental Program

Two related but distinct experimental methods have been employed to investigate metal oxides: (1) crossed-beam chemiluminescence; and (2) laser-induced fluorescence of reaction products. In the former, a beam of metal atoms traverses a scattering chamber filled with oxidizer gas where it reacts to

produce electronically-excited products. The chemiluminescence is then analyzed spectroscopically so that the internal-state distribution of the metal oxide product can be determined. In the latter, a beam of metal atoms collide with a beam of oxidizer gas to form the metal oxide product that is vibrationally and rotationally excited but electronically unexcited. Simultaneously the output of a pulsed, tunable dye laser is swept in frequency. Whenever, the dye laser frequency coincides with an absorption line of the metal oxide molecule, the molecule is excited to fluoresce, and the fluorescent signal provides a measure of the initial (v'', J'') population of the freshly formed metal oxide product.

The crossed-beam chemiluminescence apparatus, called LABSTAR, has been described previously.^{1,2} Briefly, a metal beam is formed by effusion from a molybdenum oven heated with a three-phase molybdenum-wire resistance winding. A series of heat shields and a water-cooled copper shield surround the oven and provide part of the collimation of the beam. Alternatively, the metal source in LABSTAR is a crucible placed inside a resistance-heated graphite cylinder. Although this permitted much higher temperatures, the limited capacity of the crucible prevented extended runs. All work on the group IIA metals was carried out

with the molybdenum oven; all work on aluminum used a stainless steel crucible placed inside the graphite heating element.

In both cases, the oven source is differentially pumped. A Granville-Phillips film-thickness monitor is used to measure the beam flux. Typical beam intensities in the reaction region are 10^{15} atoms/sec.

The gas source is commercial O₂, NO₂, or N₂O. In the case of ozone studies, a Welsbach ozinator is used to generate the ozone that is trapped on silica gel.

For spectroscopic work we use either a 2-m SPEX 1702 spectrometer or a 1-m Interactive Technology Inc. spectrometer. A cooled S-20 photomultiplier in conjunction with a Keithley 417 picoammeter drives a Leeds and Northrup strip-chart recorder which provides a record of the chemiluminescent spectrum.

In the laser-induced fluorescence studies of reaction products,³ the same LABSTAR configuration is used with the addition of two arms to permit the laser beam to intersect the reaction region. The laser is a modified AVCO dial-a-line laser in which a pulsed nitrogen laser pumps an organic dye solution. We have placed a beam expander in the dye laser cavity. In addition we use an eschelle grating (3600 lines/mm) operated in eighth order. With this setup we obtain a narrowing of the dye laser

output from 20 Å to 0.2 Å.

The metal oxide fluorescence is detected with gated electronics using a Keithley fast boxcar integrator. A delay of about 20 nsec is applied to the opening of the gate to remove effectively scattered laser light. The gate is maintained open several excited-state lifetimes. Alternatively, by using a narrow gate width, the metal oxide radiative decay is followed as a function of time. The latter mode permits the excited-state lifetime of the metal oxide molecule to be measured.

C. Results to Date

Crossed-Beam Chemiluminescence:

(1) Ba + NO₂ yields the BaO A - X band system (See Fig. 1) from which a lower limit to the BaO dissociation is

$$D_0^0(\text{BaO}) \geq 5.74 \text{ eV}$$

(2) Ba + N₂O has a visible band system the same as Ba + O₃. Arguments are presented that these are triplet bands (See Fig. 2)

(3) The reactions of group IIA metals with NO₂, N₂O, and

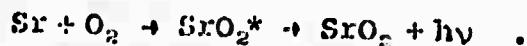
O_3 proceed with little or no activation energy.

(4) A high-resolution study (See Fig. 3) of the BaO $A - X$ bands shows that the molecules are rotationally hotter when they are vibrationally colder and vice versa.

(5) The BaO chemiluminescence of $Ba + NO_2$ is slightly polarized with the LABSTAR configuration. A theory is developed concerning the partitioning of angular momentum into internal and translational degrees of freedom of the products that accounts for the experimental observations.

(6) The cross sections for $Ba + NO_2$ are quite large ($\approx 165 \text{ } \mu\text{m}^2$) while $Ba + N_2O$ is less than gas kinetic.

(7) Sr does not react with O_3 to form SrO under thermal conditions; however, evidence is found for two-body radiative association



Two-body radiative association is found to provide the dominant visible emission⁴ in the reaction $Ba + Cl_2$ (See Fig. 4).

(8) The chemiluminescence reaction $Al + O_3$ yields the AlO $B ^3\Sigma^+ - X ^2\Sigma^+$ blue-green bands. This reaction is so exothermic that several new band heads are identified, in particular

the (17,13) at 4378 Å, the (17,14) at 4534 Å, the (17,15) at 4706 Å, the (18,14) at 4384 Å, the (18,15) at 4545 Å, the (18,16) at 4716 Å, the (13,9) at 4325 Å, the (14,12) at 4674 Å, the (15,12) at 4681 Å, the (06,13) at 4523 Å, and the (16,14) at 4694 Å. See Fig. 5.

(9) From the highest v' levels that are populated of the AlO B state, a lower limit to the AlO dissociation energy is deduced:

$$D_g^0(\text{AlO}) \geq 5.13 \pm 0.05 \text{ eV} .$$

With McDonald and Innes' reinterpretation⁵ of Tyte's continuum absorption onset to give an upper limit of $D_g^0(\text{AlO}) \leq 5.20 \pm 0.01 \text{ eV}$ we recommend⁶ the value

$$D_g^0(\text{AlO}) = 5.15 \pm 0.05 \text{ eV} .$$

(10) The AlO B - A branching is at least an order of magnitude weaker than the B - X transition.

Laser-Induced Fluorescence of Reaction Products:

(1) The method is feasible (See Fig. 6). It is possible to learn about the (v'', δ'') distribution of BaO formed in the reaction $\text{Ba} + \text{O}_2$.

(2) In the reaction $\text{Na} + \text{O}_2$, most of the reaction exothermicity goes into translational energy rather than into internal excitation. This is opposite to the conclusions reached by Connovici and Michel⁷ from their angular distribution studies.

(3) The vibrational distribution follows a Maxwell-Boltzmann distribution with a temperature of about 2500° K.

(4) The $\text{NaO} \Lambda$ state for $v' \geq 3$ has a radiative lifetime of 350 ± 50 nsec, in reasonable agreement with the recent measurements of Johnson.⁸

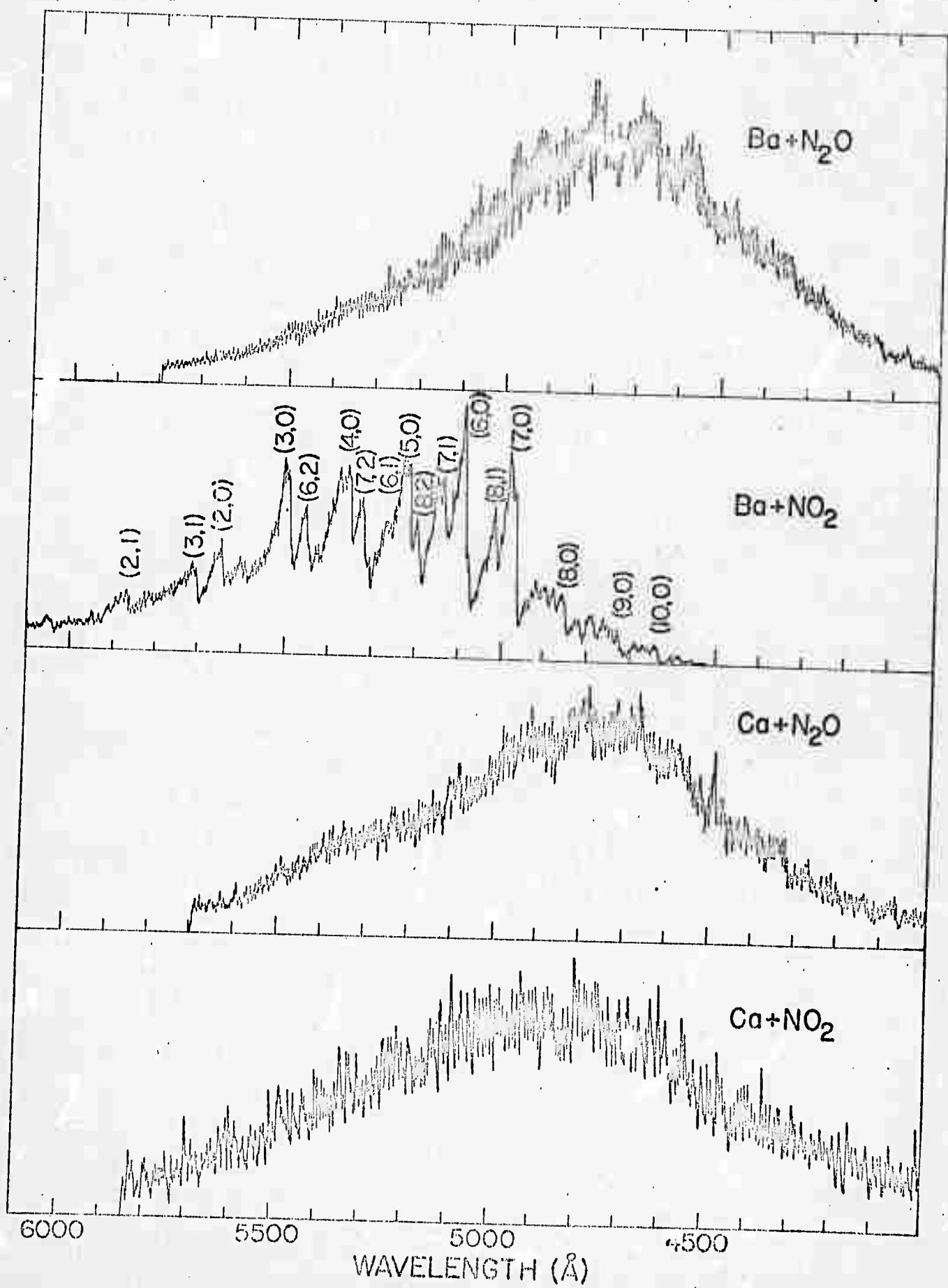
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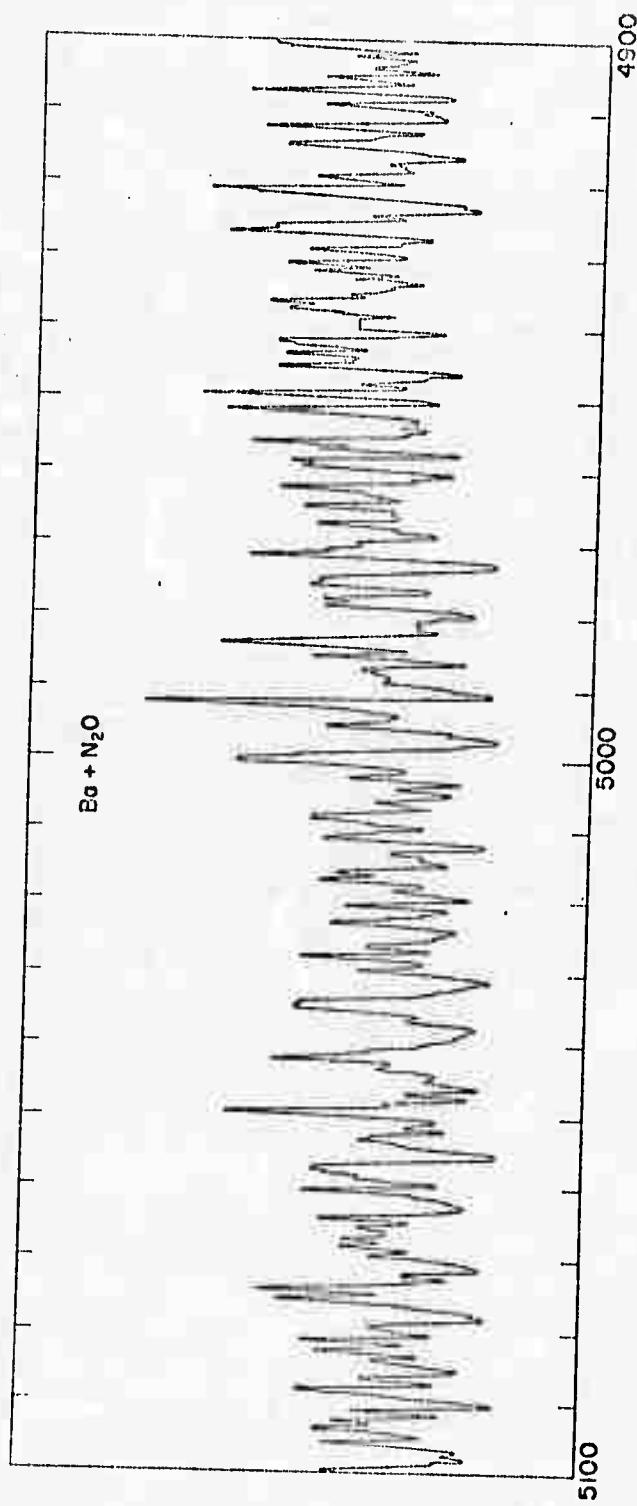
1. Ch. Ottlinger and R. N. Zare, Chem. Phys. Letters 5, 243 (1970).
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4. C. D. Jonah and R. N. Zare, Chem. Phys. Letters 9, 65 (1971).
5. J. K. McDonald and K. K. Innes, J. Mol. Spectry. 32, 501 (1969).
6. J. L. Gole and R. N. Zare, "Determination of D_0^0 ($\Lambda\delta O$) from Crossed-Beam Chemiluminescence of $\Lambda L + O_3$," J. Chem. Phys. (accepted for publication).
7. C. Batalli-Cosmovici and K. W. Michel, Chem. Phys. Letters 11, 245 (1971).
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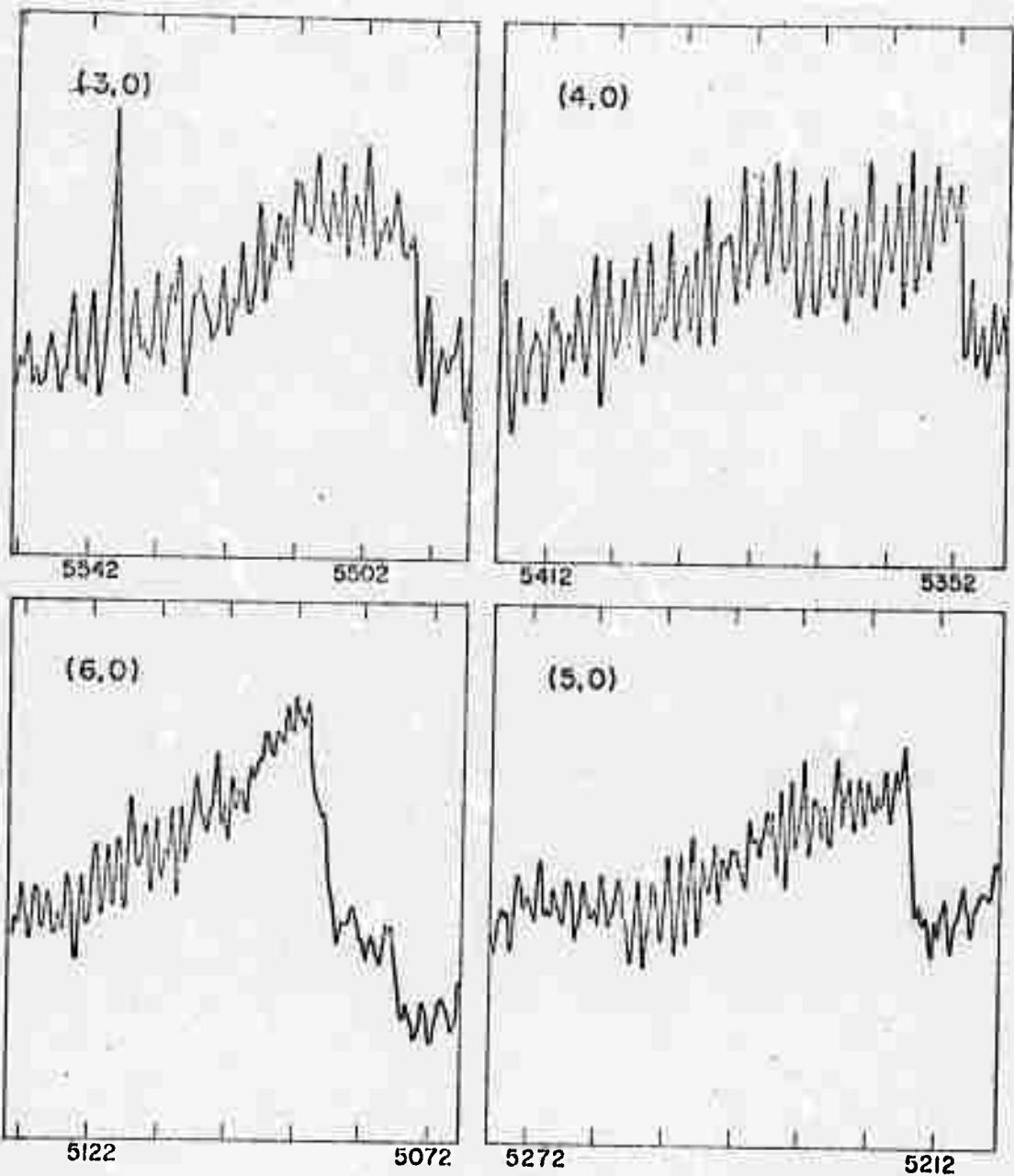
FIGURE CAPTIONS

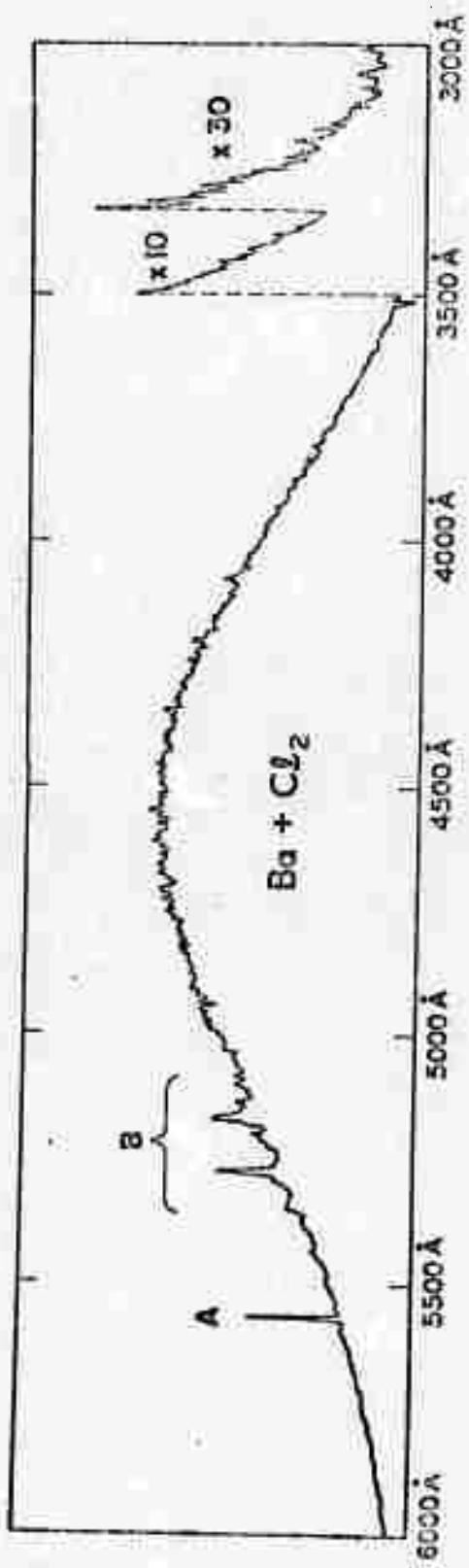
- Fig. 1. Chemiluminescent spectra. These spectra were taken with the $\frac{1}{2}$ -m Heathkit spectrometer.
- Fig. 2. Chemiluminescent spectrum of Ba + N₂O at 0.5 - Å spectral slitwidth showing its highly structured nature.
- Fig. 3. Four (v' , v'') bands from the chemiluminescent spectrum of Ba + NO₂ which show how the shading changes with v' . In the (3,0) band the 5535 - Å Ba line is present.
- Fig. 4. Spectrum of chemiluminescence from the reaction Ba + Cl₂: The letter A represents the 6s6p $^1p^0$ - 6s² 1S Ba-resonance line and the letter B represents the BaCl-emission bands (the $^2\Pi$ - $^2\Sigma$ green system). The featureless emission from 2900 to 6000 Å is assigned to emission from an excited electronic state of BaCl₂.
- Fig. 5. AlO B $^2\Sigma^+$ - X $^2\Sigma^+$ chemiluminescent emission from the reaction Al + O₂. The band heads are designated by (v' , v'').
- Fig. 6. The BaO fluorescence signal as a function of laser wavelength: (a) fast scan showing vibrational

(6) distribution; (b) slow scan showing rotational distribution of the (3,0) band. The asterisks mark a perturbation.

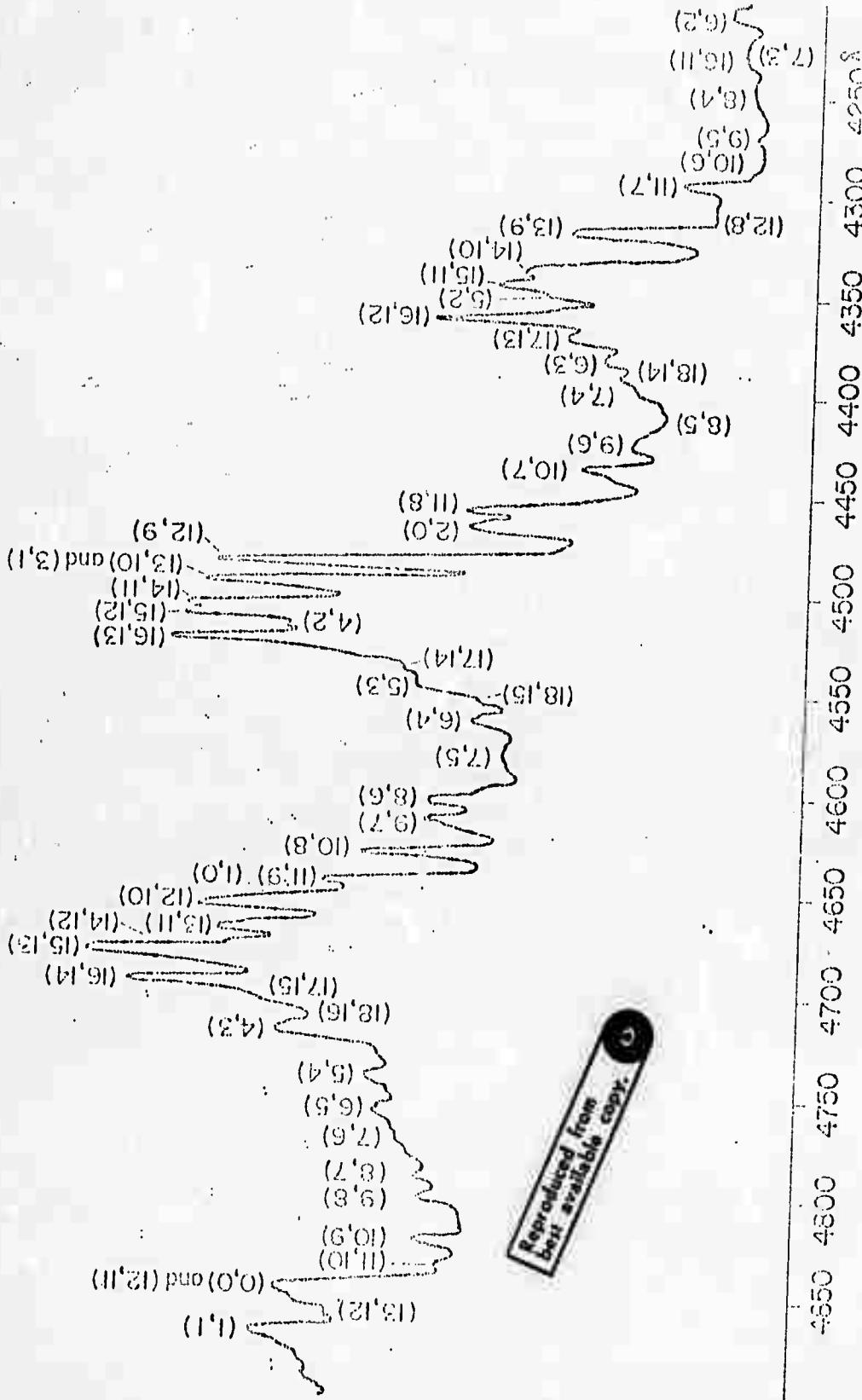


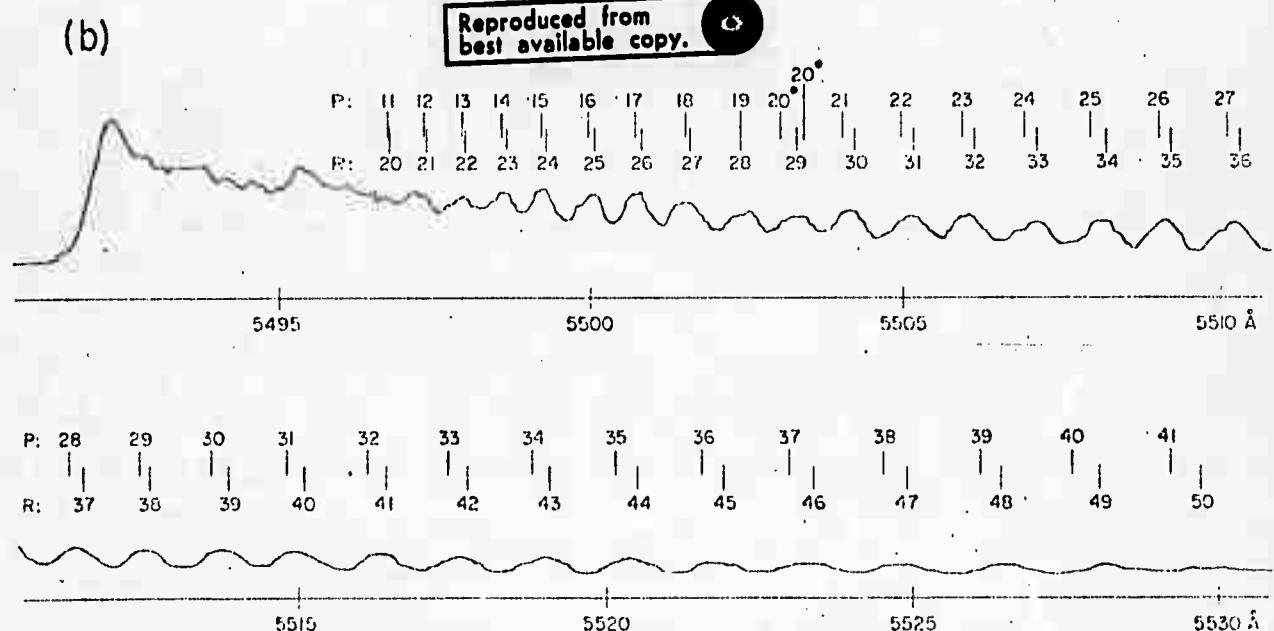
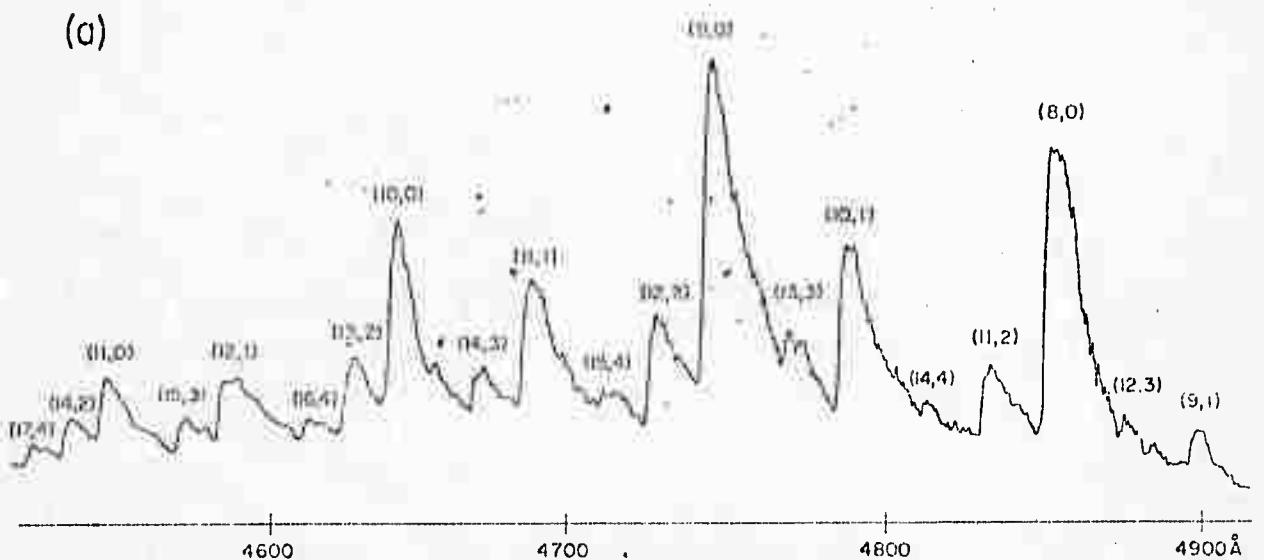






ALO CHEMILUMINESCENT SPECTRUM
 $B^2\Sigma^+ - X^2\Sigma^+$





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